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Low-Magnetic Field Effect and Electrically Detected Magnetic Resonance Measurements of Photocurrent in Vacuum Vapor Deposition Films of Weak Charge-Transfer Pyrene/Dimethylpyromellitimide (Py/ DMPI) Complex

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ABSTRACT

Magnetic field effect (MFE) and electrically-detected magnetic resonance (EDMR) measurements of photocurrent have been conducted to clarify the excited-state dynamics in films of an organic weak charge-transfer (CT) complex, Pyrene/Dimethyl-pyromellitimide (Py/DMPi), fabricated by vacuum vapor deposition (VVD). Low-field MFE measurements of the photocurrent were carried out using an interdigitated platinum electrode made on a quartz substrate as well as the re-examination of the photocurrent and MFE in the range of 3–200 mT. The spin-dependent carrier dynamics leading to the low-field MFE are reasonably simulated as the low-field effect due to the hyperfine mechanism in the radical-pair intersystem crossing, which was solved through the Liouville equations of the density matrix for the stepwise hopping model in the doublet electron-hole pair (DD pair mechanism). Single-crystal time-resolved electron spin resonance (TRESR) measurement was also carried out to justify the MFE mechanism. Averaged trap depth (E_{trap}) of the triplet exciton was estimated to be $+640 \pm 89 \text{ cm}^{-1}$ ($E_{\text{trap}}/k_B = +921 \pm 128 \text{ K}$) by the temperature dependence of the signal intensity. This finding gave the confidential experimental evidence for the majority of the trapped triplet exciton (^3ext). EDMR experiment directly revealed the evidence of the weakly coupled electron-hole pairs. The effective activation energies (ΔE) for the separation from the photoinduced CT state to the mobile carriers is $1200 - 1900 \text{ cm}^{-1}$ ($\Delta E/k_B = 1700 - 2700 \text{ K}$). A systematic protocol to clarify the photo-generated carrier dynamics in weak CT complexes is demonstrated, and our findings from this method give not only the further support for the two types of collision mechanisms assumed in our previous work but also the detailed information of the carrier dynamics of the weak CT complex, including the activation energy and trapping/de-trapping process, which give significant influence on the performance of the organic devices.

I. INTRODUCTION

Thin organic-semiconductor films have been largely studied as promising materials for organic light emitting diodes (OLEDs),^{1, 2} organic field effect transistors (OFETs),³ and organic solar cells (OSCs).⁴ Organic semiconductors offer many advantageous features, because they are thin and flexible substrates and can be fabricated through the cost-efficient method of ink-jet printing. Charge transfer (CT) states known as polaron pair (weakly coupled intermolecular electron-hole pair) and the charge migration in their devices play significantly important role for the performance of the OLED and OSC devices. Carrier dynamics including trapping and collision process of the charge carriers gives direct influence on the charge migration. The excited-state dynamics leading to the carrier generation and the electron-hole charge recombination is also an important process in their devices. In addition, the physical properties immediately after photoexcitation of molecular CT complexes are of interest in the context of ultra-fast photoinduced metal-insulator transition of organic salts, (EDO-TTF)₂PF₆, within 20 fs at room temperature.⁵ Photocurrent behavior of weak molecular CT complexes was also studied to use as a molecular conductor with photo-controllable localized spin⁶ and to demonstrate the memory effect in photoinduced conductive switching.⁷

Therefore, the photophysical properties of weak organic CT complexes is an important area to investigate. The photoconductivity of the organic CT complexes was intensively studied using single crystals (over 20 years ago) in the researches of CT exciton, triplet-triplet annihilation and molecular electronics.⁸ However, single crystals are unsuitable for device fabrication. Thermal evaporation is a facile method for device fabrication. The morphology of the vacuum vapor deposition (VVD) films affects the carrier dynamics. Therefore, re-examination of photocurrent behavior and the carrier dynamics in the VVD films of organic weak CT complexes is worthy of the investigation. Magnetic field effect (MFE) in electronic conductance or photo-emission is a characteristic property, arising from the diffusion of polarized spin carriers. The mechanism of the MFE has been well established by a lot of works concerned with the radical pairs.⁹⁻¹⁰ Therefore, the observation of MFE is one of the powerful tools to clarify the carrier dynamics in their devices.¹¹⁻¹² MFE in organic thin-film devices, such as OLEDs,¹³ organic semiconductors,¹⁴⁻¹⁷ solar cells,^{11, 18-20} have received considerable attention for the last decade. In our previous work,²¹ we reported the photoconductivity and the MFE in VVD films of organic weak CT complexes using pyrene/dimethylpyromellitimide (Py/DMPI, Figure 1) or pyrene/pyromellitic dianhydride (Py/PMDA). These materials are ideal to study the carrier dynamics of the

photocurrent and the excited-state dynamics to the carrier generation because their donor and acceptor properties have been well examined and their molecular stoichiometry is well defined. Although the photoconductivity of Py/DMPI was previously reported in single crystals in 1977,²² we examined the photoconductivity and the MFE in VVD films. We measured the MFE of the photocurrent, i.e. the magneto-photoconductivity (MPC), in the field-region ($3 < B < 200$ mT). The MPC was simulated by assuming two collision mechanisms between the electron and hole carriers and between the trapped triplet excitons and mobile carriers.

In this work, we report the electrically detected magnetic resonance (EDMR) of photo-conductivity, temperature dependence of the time-resolved electron spin resonance (TRESR) as well as the MPC measurements in the low-field region using the VVD films of the organic weak CT complex, Py/DMPI. Combination of these measurements provide the detailed information about the weakly coupled electron-hole pair and the carrier dynamics in the VVD films including the trap depth and the activation energy to the carrier generation. They will give the fundamental knowledges to understanding the organic electronics devices. Trap depth of the triplet exciton and effective activation energies from the photoinduced CT state to the mobile carries are estimated by the temperature dependence. The detailed spin-dependent carrier dynamics is revealed by the low-field MPC and the quantum-dynamics simulation using stochastic Liouville equation of the stepwise carrier hopping model. It is clarified that the low-field MPC is originated from the low-field effect due to the hyperfine interaction,^{23 24 25 26 27 28} leading to the radical-pair ISC within the weakly coupled electron-hole pair and the effective hyperfine splitting estimated by the comparison between the simulation and the observed low-field MPC. In addition, this work provides confidential experimental evidence supporting the two types of collision mechanisms described in our previous work.²¹

II. EXCITED-STATE DYNAMICS

The excited-state and carrier dynamics proposed in our previous work²¹ is shown in Figure. 2(a). In this figure, D^+ and A^- denote the cation radical of pyrene and anion radical of DMPI, respectively. When the cation radical of pyrene (D^+) move in the VVD film by hopping to the nearest pyrene unit, it carries the spin-doublet positive charge (hole; h^+). The spin-doublet negative charge (electron; e^-) is carried when the anion radical of DMPI (A^-) hops in the film. The ^3ex and $^3\text{ex}_t$ express the moving triplet exciton and the trapped one, respectively. The triplet exciton was due to the triplet-state of pyrene within the CT complex, judging from the fine-structure splitting observed in

TRESR—which moves among adjacent pyrene molecules by hopping at room temperature.²¹ In the previous work, a positive MPC was observed in the field-region ($3 < B < 200$ mT). The MPC behaviour could be explained by two types of collision mechanisms: collision between the spin-doublet electron (2e) and spin-doublet hole (2h) carriers—DD pair mechanism—and collision between the trapped triplet excitons (3ex_t) and mobile doublet carriers (3c)—TD pair mechanism. The observed positive MPC in the field region lower than 10 mT could be explained dominantly by radical-pair intersystem crossing (ISC) in the DD pair ($^2e - ^2h$ pair). However, the total magnitude of the MPC in this low-field region was unknown, because of the lack of the MPC data lower than 3 mT. The observed positive MPC in the field region higher than 20 mT was explained by the radical-triplet pair ISC under the external magnetic field within the TD pair ($^3ex - ^2c$ pair). The collision of the mobile carrier (2c) to the trapped triplet exciton (3ex_t) leads to the trapping of the mobile carrier. This effect decreases the photocurrent. On the contrary, the collision of the trapped carrier (2c_t) to the mobile triplet exciton (3ex) leads to the increase of the photocurrent. Since the deactivation from $^2(ex-c)$ to the ground state occurs spin-selectively (see Fig. 2), the radical-triplet pair ISC leads to the positive MPC in the former case and to the negative MPC in the latter case. In this TD pair mechanism, the majority of the triplet excitons should be trapped to give the observed positive MPC. The total magnitude of the low-field MPC and the direct evidence of the majority of the trapped exciton will be shown later. The relationship between the energy level locations and the activation energies are depicted in Fig. 2(b). Their ΔE and E_{trap} will be also evaluated in this work.

III. METHODS

A. Sample preparation

The VVD films of Py/DMPI were fabricated on a custom-made interdigitated platinum electrode (Tohnic Inc., substrate: quartz, 125 x 2 digits, digit length: 0.5 mm, gap: 10 mm, thickness: 150 ± 15 nm (Pt) with 40 ± 4 nm (Ti)) using a resistance-heating-type vacuum evaporation apparatus (Sanyu Electron SVC-700TM/700-2). The grinded Py/DMPI crystals were used as the materials in the vapor deposition.

B. Measurements

The temperature dependence of the photocurrent was measured under the residual magnetic field (~ 3 mT) of an iron-core magnet. MFE measurements of photocurrent

(MPC) were performed on a system built in our laboratory. The photocurrent was detected under a voltage bias using a picoammeter (KEITHLEY, Picoammeter/Voltage Source 6487) under illumination from a Xenon lamp (USHIO, UI-501C) followed by a 5 cm pass-length water filter and an UV-vis liquid optical light guide. In the low-field effect experiments, the magnetic field was applied using a Helmholtz coil (GIGATECO) with DC power supplies (Keysight E3633A). The magnetic flux density was measured using a Gaussmeter (TOYO Corporation, Bell 5170). In the higher field experiments, the iron-core magnet from an X-band ESR apparatus was used. The measurements were carried out at room temperature under a nitrogen gas atmosphere to prevent degradation of the thin films. The MPC in the low-field region was measured by cycling the applied magnetic field from 0–10 mT at intervals of 0.1 mT. In order to remove artefacts, the data obtained from 75 repeated field cycles was averaged. MPC data in the higher-field region (3–200 mT) was obtained by averaging 15 repeated field cycles. Both MPC data were compared in the relative MPC ratio (%).

The EDMR experiments of the photocurrent were carried out under a 1.5 V applied bias (Voltage source; MATSUSADA, P4K-36) using an X-band ESR spectrometer (JEOL, JES-TE300). A microwave amplitude was modulated with a PIN modulator connected to an arbitrary function generator (TEXIO, AFG-2012). Continuous light illumination was achieved using the same light source set-up as the MFE measurements. The photocurrent change induced by the microwave amplitude modulation was detected as the voltage change by a lock-in amplifier (Signal Recovery, model 7280) using a custom-made operational-amplifier interface circuit.

TRESR spectra were measured with a laboratory-built apparatus setup using an X-band ESR spectrometer (JEOL JES-TE300), wide-band preamplifier, high-speed digital oscilloscope (LeCroy 9350C), and Nd:YAG pulse LASER (Continuum Surelite II). Excitation was carried out at 532 nm using the 2nd harmonics of the Nd:YAG LASER. A LASER pulse of 4–7 mJ/pulse was used in the excitation.

All instruments were controlled by a computer using a program made in our laboratory using LabVIEW. The sample temperature in the photocurrent and EDMR measurements was controlled by a N₂ gas flow system (Oxford ESR900 Cryostat and Oxford, Mercury iTC). In the TRESR experiment, the sample temperature was controlled by a cooled He gas flow system (Oxford ESR910 Cryostat and Oxford, ITC503).

The time-resolved emission measurements (see the supporting information) were performed using a pulsed Nd:YAG laser (Continuum Surelite II, 355 nm, fwhm ~ 7 ns, repetition rate = 10 Hz) for an excitation light source. Sample was mounted

perpendicular to the excitation light. The emission was detected by using an ICCD camera (Princeton PI-MAX) equipped with an imaging spectrometer (Acton SpectraPro2300i).

IV. RESULTS AND DISCUSSION

A. Temperature Dependence of Photocurrent

In the present work, we used a custom-made quartz-substrate with interdigitated platinum electrodes to avoid a leak current. We found that the conduction of photo-generated carriers through the glass-substrate was larger than that through the Py/DMPI layer because of the relatively high impedance of the Py/DMPI layer. Thus, the photo-generated carrier was conducted through the glass-substrate between the platinum electrodes, when the commercially easy-available interdigitated platinum electrodes fabricated on the usual glass-substrate was used. This mitigates the influence on the MPC ratio as it is proportional to the MFE of carrier generation efficiency in the Py/DMPI layer; however, the magnitude in photocurrent was changed due to the difference of the carrier mobility between the Py/DMPI layer and the glass-substrate. Therefore, in this work, the photocurrent response and MPC in the field range of 3–200 mT were re-examined using the custom-made interdigitated platinum electrode with quartz substrate. The temperature dependence of the photocurrent was also examined in this work. Figure 3(a) shows the photocurrent response at an applied voltage bias of 10 V obtained by 30 s intervals of On/Off cycles of a white light illumination with a xenon lamp. The excitation wavelength dependence of the photocurrent is given in the supporting information (Fig. S1). The response behavior to the light illumination was similar to that of previous work.²¹ However, the absolute value was smaller by 2 orders of magnitude. This difference is due to the resistance between the Py/DMPI layer and the glass-substrate (approximately 10^{12} – 10^{14} Ω cm). In the semiconductor, the electric current density ($\mathbf{J}$) is given by $\mathbf{J}(\mathbf{r}) = q\{n(\mathbf{r})\eta\mathbf{E} + D_c\nabla n(\mathbf{r})\}$. Here, q , $n(\mathbf{r})$, η , $\mathbf{E}$, and D_c are the charge of the carrier, carrier density at $\mathbf{r}$, carrier mobility, electric field, and diffusion constant of the carrier, respectively. In the present steady-state condition of photo-illumination using a cw-lamp, the $\nabla n(\mathbf{r})$ is expected to be small (uniform excitation). Therefore, the difference of the absolute magnitude of the photocurrent is due to the first term. Thus, the η of the Py/DMPI layer was two orders smaller than that of the glass-substrate used in the interdigitated platinum electrode. The resistance of the quartz-substrate is 10^{18} Ω cm, which is much larger than that of the Py/DMPI layer. Therefore, the current behavior (Fig. 3(a)) is the intrinsic behavior of the Py/DMPI layer. Figure 3(b) shows the temperature dependence

of the photo-current intensity. This behavior was well fitted by the Arrhenius equation:

$$I = A \exp\left(-\frac{\Delta E}{k_B T}\right) + I_0 \quad (1)$$

ΔE under 10 V bias was determined to be $+1176 \pm 28 \text{ cm}^{-1}$ ($\Delta E/k_B = +1692 \pm 41 \text{ K}$) by a least-squares fit. ΔE measured under 1.5 V bias showed a similar magnitude of the activation energy, $+1047 \pm 88 \text{ cm}^{-1}$ ($\Delta E/k_B = +1507 \pm 126 \text{ K}$) (see Fig. S2). There is no significant bias dependency of the activation energy. Separation from the photoinduced CT state (D^+-A^-) to mobile carriers contains a multi-step process: (1) the formation of a weakly coupled electron-hole (DD) pair from the CT state, (2) the separation from the weakly coupled DD pair to the mobile carriers, and (3) trap and de-trap of the carriers. The effective activation energy obtained in this photocurrent measurement is the sum of the activation energy of these processes (see Fig. 2(b)). The magnitude of the activation energy (ΔE) was comparable to that in the single crystal measurement of the anthracene/pyromelliticdianhydride CT complex ($0.14 \text{ eV} = 1129 \text{ cm}^{-1}$).²⁹ It should be noted that the de-trapping of the carrier is also temperature dependent, which increases the mobile carrier with increasing temperature. Therefore, the estimated value obtained at 1200 cm^{-1} in this experiment may be evaluated as slightly lower than the effective activation energy for the separation from the photoinduced CT state (D^+-A^-) to the mobile carriers.

B. MPC in 3–200 mT

Figure 4 shows the MPC ratio observed for the Py/DMPI VVD film fabricated on the custom-made interdigitated platinum electrode using quartz substrate. This ratio is defined by Eq. (2) using the intensity of the current ($I(B)$) at the external magnetic field, B , and the $I(0)$ at zero magnetic field.

$$\text{MPC}(B) = \frac{I(B) - I(0 \text{ mT})}{I(0 \text{ mT})} \times 100 \quad (2)$$

The MPC in the field region of 3–200 mT was measured under 10 V applied bias and a white light illumination ($\sim 539 \text{ mW}$). The magnitude of the MPC was changed due to the different carrier mobility, η . However, the ratio and the curvature of the MPC vs. temperature resembled to the previous results.²¹ In order to evaluate the total ratio, the MPC data obtained at greater than 3 mT in the present experiment was converted to the values estimated from 0 mT using the following equation:

$$\text{MPC}(B) = \left(\frac{\langle I(B) \rangle - \langle I(3 \text{ mT}) \rangle}{\langle I(3 \text{ mT}) \rangle} - \frac{\langle I_l(0) \rangle - \langle I_l(3 \text{ mT}) \rangle}{\langle I_l(3 \text{ mT}) \rangle} \right) \times \frac{\langle I_l(3 \text{ mT}) \rangle}{\langle I_l(0 \text{ mT}) \rangle} \times 100 \quad (3)$$

Here, $\langle I_l(x \text{ mT}) \rangle$ means the data obtained from the low-field MFE measurements.

The MPC data in 3–200 mT were compared to those in 0–10 mT as the relative MPC ratio (%) as shown in Fig. 4. The total ratio of MPC was found to be increased by approximately 3.7% of the photocurrent at 200 mT.

C. Low-Field Effect of MPC

Figure 5 shows the results of the MPC measurement and simulation in the low-field region of 0–10 mT. The ratio of the MPC was measured under a 10 V applied bias and a white light illumination (~ 539 mW). A small dip was observed at approximately 0.3 mT, suggesting the low-field effect by a hyperfine interaction^{23 24 25 26 27 28} or a small exchange interaction^{30 31 32} in the electron-hole carrier pairs. The carrier dynamics of the spin-doublet electron-hole pair (DD pair) is shown in Fig. 2. In the present system, either of electron or hole acts as the mobile carrier and the other is trapped or acts as a slow mobile carrier. It is difficult to discern which is the mobile carrier, because the experiment to determine the sign of the charge in the mobile carrier has not been carried out. In our previous experiment,²¹ there was a lack of experimental data in the very low-field region and some unknown parameters such as the hyperfine splitting (they were estimated by using the molecular orbital calculation), making it difficult to define the total magnitude of the MPC effect. However, in the low-field MPC experiment shown in Fig. 5, we could obtain the data to discuss the total magnitude of the low-field effect. Furthermore, the small dip at ca. 0.3 mT will give the information of the hyperfine coupling or the small exchange interaction. Therefore, we tried to reproduce the magnitude and shape of the low-field MFE by the simulation using stochastic Liouville equations of the DD pair. Since the carriers (electron or hole) are moving in the VVD film by hopping to the adjacent molecules (DMPI or pyrene) as shown in Fig. 6(a), stepwise electron or hole hopping model shown in Fig. 6(c) is a sophisticated model in the present Py/DMPI CT complex. It should be noted that the nearest neighbor contact (closest contact) electron-hole pair (D0 – D1 pair in Fig. 6(c)) within the excited CT complex $^1(D^+ - A^-)$ does not contribute to the MPC because of the large energy splitting between the singlet ($^1(D^+ - A^-)$) and triplet ($^3(D^+ - A^-)$) states induced by the large exchange coupling. Therefore, in the previous work,²¹ the shape of the MPC curve in the DD mechanism was simulated for the second neighbor contact e-h pair (D0 – D2 pair in Fig. 6(a)) and assumed the spin-selective transfer by the charge-recombination (CR) to the ground-state ($^1(D^{\delta+} - A^{\delta-})$) and the ISC to the triplet excitonic state of pyrene. However, the CR and the ISC are expected to occur effectively within the nearest neighbour contact pair (D0 – D1 pair in Fig. 6(c), $^1(D^+ - A^-)$) as shown in Fig. 6(b). They do not occur effectively in the D0 – D2 pair. Therefore, the

stepwise hopping model shown in Fig. 6(c) is more sophisticated model than that used in the previous work. Since this hopping model express the actual situation without contradiction, one can discuss the total ratio of the MPC. The stepwise hopping model can be expressed by the simultaneous stochastic Liouville equations of the density matrix,^{30 31 32} which are given by:

$$\begin{aligned} \frac{d\rho_{D0D1}(t)}{dt} = & -\frac{i}{\hbar}[\mathbf{H}_{D0D1}, \rho_{D0D1}(t)] + k_0\rho_{D0D1}(0) - k_{-1}\rho_{D0D1}(t) - \frac{k_S}{2}(\rho_{D0D1}(t)\mathbf{A}_S + \mathbf{A}_S\rho_{D0D1}(t)) \\ & - \frac{k_T}{2}(\rho_{D0D1}(t)\mathbf{A}_T + \mathbf{A}_T\rho_{D0D1}(t)), \end{aligned} \quad (4)$$

$$\frac{d\rho_{D0D2}(t)}{dt} = -\frac{i}{\hbar}[\mathbf{H}_{D0D2}, \rho_{D0D2}(t)] + k_1\rho_{D0D1}(0) - k_{-1}\rho_{D0D2}(t) - k_1\rho_{D0D2}(t) + k_{-1}\rho_{D0D3}(t), \quad (5)$$

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$$\frac{d\rho_{D0Dn}(t)}{dt} = -\frac{i}{\hbar}[\mathbf{H}_{D0Dn}, \rho_{D0Dn}(t)] + k_1\rho_{D0Dn-1}(0) - k_{-1}\rho_{D0Dn}(t) - k_1\rho_{D0Dn}(t). \quad (6)$$

where

$$\begin{aligned} \mathbf{H}_{D0Dm} = & g_{D0}\mu_B\mathbf{B} \cdot \mathbf{S}_{D0} + g_{Dm}\mu_B\mathbf{B} \cdot \mathbf{S}_{Dm} + \mathbf{S}_{D0m}^T \cdot \mathbf{D} \cdot \mathbf{S}_{D0m}^T + a_{D0}^{eff}\mathbf{S}_{D0} \cdot \mathbf{I}_{D0} \\ & + a_{Dm}^{eff}\mathbf{S}_{Dm} \cdot \mathbf{I}_{Dm} - 2J_{D0Dm}\mathbf{S}_{D0} \cdot \mathbf{S}_{Dm} \quad (\mathbf{S}_{D0m}^T = \mathbf{S}_{D0} + \mathbf{S}_{Dm}) \end{aligned} \quad (7)$$

and

$$\mathbf{A}_S = |S\rangle\langle S|, \quad (8)$$

$$\mathbf{A}_T = \sum_i |T_i\rangle\langle T_i| \quad (9) \quad (\text{in the eigenfunction basis of } \mathcal{S}^2 \text{ operator})$$

Here, $\rho_{D0Dm}(t)$ is the density matrix of the DD pair between D0 and Dm sites at time t . $g_{Di}\mu_B\mathbf{B} \cdot \mathbf{S}_{Dm}$, $\mathbf{S}_{D0m}^T \cdot \mathbf{D} \cdot \mathbf{S}_{D0m}^T$, $a_{Dm}^{eff}\mathbf{S}_{Dm} \cdot \mathbf{I}_{Dm}$, and $-2J_{D0Dm}\mathbf{S}_{D0} \cdot \mathbf{S}_{Dm}$ are Zeeman, the fine-structure, and averaged hyperfine interaction of the Dm site, and exchange interaction between the D0 and Dm sites, respectively. $\mathbf{A}_S$ and $\mathbf{A}_T$ are projection operators on the singlet and triplet spin states of the D0–D1 pair. $\rho_{D0D1}(0)$ is the initial condition at time zero by the photoexcitation, which corresponds to the density matrix of the geminate D0–D1 pair. The selective population to the singlet configuration ($^1(e^-h^+)$) in the nearest neighbor contact electron-hole pair was assumed as the $\rho_{D0D1}(0)$, because the charge separated singlet excited states, ($^1(D^+ - A^-)$), are effectively generated by the direct photoexcitation of the CT band in such weak CT complex. k_0 is the rate constant of the photoexcitation. k_1 , k_{-1} , k_S , and k_T are the rate constants for

each process depicted in Fig. 6. H_{D0Dm} is the spin Hamiltonian for the m -th neighbor contact DD pair (D0–D m pair). The last term in the right side of Eq. (6), $-k_1 \rho_{D0Dn}(t)$, leads to the photocurrent. The third, fourth, fifth, and so-forth neighbor contact pairs contribute to the MPC in addition to the second neighbor contact pair.^{30 31 32}

In this model, it is assumed that the hole (or electron) hops to the nearest pyrene unit (or DMPI unit) with the same rate constants of k_1 and k_{-1} . The rate constant of k_{-1} can be reasonably assumed to be same as k_1 , because the process is the charge migration as shown in Fig. 6(a) by the hopping mechanism. As shown in Fig. 6(a), only the relative distance between the cation radical of pyrene (D^+) and the anion radical of DMPI (A^-) is important, although it is depicted in Fig. 6(c) that the species A^- (D^+) seem to be separating from another species D^+ (A^-). The spin selective CR to the ground-state occurs from the singlet spin configuration of the D0–D1 pair, that is, $^1(D^+-A^-)$, because the ground-state of the CT complex is the $^1(D^{\delta+}-A^{\delta-})$ state [singlet channel]. The ISC pathway to the triplet excited state of pyrene in the CT complex, $^3(D^*-A)$, is also effective only from the D0–D1, $^1(D^+-A^-)$, as shown in Fig. 6(b) [triplet channel]. The low-field MPC was simulated by solving the simultaneous Liouville equations (4) – (6) expressing the stepwise hopping model. The details of the simulation procedures are given in the appendix. In the spin Hamiltonian (7), the summation of hyperfine terms for each nucleus in the D0 and D m sites was approximated as an isotropic effective hyperfine coupling as follows:

$$\sum_i S_{D0} \cdot A_i \cdot I_{D0i} \rightarrow a_{D0}^{eff} S_{D0} \cdot I_{D1}, \quad \sum_j S_{D2} \cdot A_j \cdot I_{D2j} \rightarrow a_{D2}^{eff} S_{D2} \cdot I_{D2}. \quad (10)$$

From the DFT calculations in our previous study, the effective isotropic hyperfine-couplings of the cation radical of pyrene and the anion radical of DMPI were estimated to be $a_{D0}^{eff} = -30$ MHz (pyrene cation; D^+) and $a_{D2}^{eff} = -8$ MHz (DMPI anion; A^-), respectively.²¹ In this work, the magnitudes of a_{D0}^{eff} and a_{D2}^{eff} were varied from the estimated values to reproduce both the observed dip position and the overall MPC in the low-field region. It was difficult to determine these values as a unique solution because there was ambiguity to the parameter fits. The values of a_{D0}^{eff} and a_{D2}^{eff} were determined to be -26 MHz and -14 MHz, respectively (one possible set values). The simulation curve, shown in blue, reproduced the observed MFE in the low field region and the field position of the dip. As discussed in our previous study, the MPC curve in the higher field region could be simulated by a collision model between the trapped triplet exciton and mobile carrier (TD model). However, since the low-field MFE behavior is almost reproduced by the present stepwise hopping DD pair model as shown in Fig. 5, the contribution from the TD model is expected to be smaller than that

assumed in our previous work.²¹ The slight difference between the observed and simulated curves may come from the approximation, where the relative orientations among the fine-structure tensors of each contact sites are ignored and some of the parameters are estimated ones not determined precisely by the experiments (see the supporting information). In addition, although we chose the simulation of 8 interacting sites, the MPC ratio (2.1 %) at 10 mT will be expected to increase to ca. 2.6% (see Fig. 9(b) in Appendix). Although the fit of these parameters does not yield a unique solution, the effective hyperfine couplings in this CT system were determined from the dip field. These results show that the observed low-field MPC is due to the hyperfine mechanism leading to the radical-pair ISC within the DD pair.^{23 24 25 26 27 28}

D. Results of EDMR Measurement

Figure 7(a) shows an EDMR signal observed at room temperature by monitoring the photocurrent of the Py/DMPI VVD film. A single peak was observed in the magnetic field at $g = 2.0034$, which defers slightly from the g value of a free-electron. During this measurement, a phase-sensitive detection of voltage change due to microwave amplitude modulation was carried out by a lock-in amplifier. The line-shape was analyzed by the Lorentzian equation, which indicated that the signal originated from the mobile species. It should be noted that a non-interacting electron or hole carrier cannot change the photocurrent intensity through a microwave transition between the spin sublevels of their doublet state. The EDMR signals of photocurrent for a tetracene layer deposited by vacuum sublimation and for the polycrystalline samples of anthracene-tetracyanobenzene CT complexes were originally reported in the 1970s.^{33 34} In these works, the mechanism of the EDMR signal generation was explained by the microwave induced population changes between the triplet-state spin sublevels of the photoinduced CT state (D^+A^-) combined with $S-T_0$ mixing (radical-pair ISC).^{33 35} A similar mechanism is expected in the photoexcited states of Py/DMPI VVD films (the inset in Fig. 7(b)). The observed signal in Fig. 7(a) was single peak without any splitting, showing the negligible fine-structure term in the detected triplet-state. Therefore, the observation of the EDMR signal gives direct evidence of the weakly coupled electron-hole pair, which dissolves into mobile carriers. The electron and hole dissolved from the photoinduced CT state (D^+-A^-) forms the weakly coupled DD pair, which contributes to EDMR signal generation. From the linewidth ($\delta H = 1.4$ mT) of the EDMR signal (Lorentzian line shape), the lifetime (τ) of the weakly coupled DD pair was estimated to be 4.0×10^{-9} s using relationship of $\delta H \sim \hbar/g\beta\tau$. This lifetime was close to that (7.0×10^{-9} s) of the tetracene layer deposited by vacuum sublimation estimated by the same procedure.³⁵ From the lifetime, the dissociation kinetic constants of the

weakly coupled DD pair (k_1 and k_{-1}) were estimated to be $k_1 = k_{-1} = 1.0 \times 10^8 \text{ s}^{-1}$ as described in the supporting information. The temperature dependence of the signal intensity (Fig. 7(b)) could be analyzed well by the Arrhenius equation (1). The corresponding EDMR spectra observed at each temperature are given in the supporting information (Fig. S3). The ΔE value was estimated to be $+1868 \pm 204 \text{ cm}^{-1}$ ($\Delta E/k_B = +2688 \pm 294 \text{ K}$) by the least-squares fit. This ΔE is corresponding to the activation energy (ΔE) from $^1(\text{D}^+-\text{A}^-)$ to the mobile carriers shown in Fig. 6(b), because $I(T)_{\text{EDMR}} = C \exp(-\Delta E_1/k_B T) \exp(-\Delta E_2/k_B T)$ (negligible initial population in $^3(\text{D}^+-\text{A}^-)$). However, the magnitude is slightly over-estimated due to the spin-lattice relaxation effect, which decreases EDMR signal intensity, and/or the small signal-to-noise ratio. Actually, the estimated value of approximately $+1900 \text{ cm}^{-1}$ (over-estimate) in this experiment is a little larger than $+1200 \text{ cm}^{-1}$ (under-estimate) estimated from the temperature dependence of the photocurrent. Therefore, the actual effective activation energy for separation into the mobile carriers is evaluated to lie between these values. Direct detection of the signal without the phase-sensitive detection technique was not succeeded for this VVD film. Direct detection of the EDMR signal will yield additional information on the sign of the photocurrent change, depending on the relative relation ($k_T > k_S$ or $k_T < k_S$) between the kinetic processes (k_T and k_S in Fig. 6) to the triplet excitonic state and to the ground state. Furthermore, if time-resolved EDMR measurement using the direct signal detection is possible, it will give further information about the effective kinetic constant of mobile carrier formation. Although our trial was failed in the present VVD films of Py/DMPI, the time-resolved EDMR can be in principle possible using pulsed laser excitation and fast direct detection of the photocurrent response to the microwave (the difference between ON and OFF condition of the microwave). In the present work, the kinetic constants were not directly determined by experiment. They were evaluated from the EDMR linewidth and the lifetime of the luminescence with the help of the simulation (see the supporting information). The time profile of the time-resolved EDMR contains the direct information of the dissociation kinetic constant (k_1 and k_{-1}) and the intensity contains the information about the ratio of the rate constants (k_T/k_S and k_1) indirectly. If the time-resolved EDMR experiment is succeeded, the dissociation kinetic constant (k_1 and k_{-1}) can be experimentally evaluated directly by the fitting of the decay of the signals as a similar manner to the time-resolved optically detected magnetic resonance experiments in our previous work of a luminescent π -radical.³⁶

E. Temperature Dependence of Single-Crystal TRESR

The powder-pattern TRESR spectrum was reported in our previous work.²¹ The

spin Hamiltonian parameters of the mobile triplet exciton were determined to be $g = 2.005$ (isotropic), $D = 0.0830 \text{ cm}^{-1}$, and $E = 0.0160 \text{ cm}^{-1}$, as well as the relative populations in the zero-field spin sublevels ($P_x = 0.00$, $P_y = 0.92$, $P_z = 0.08$) from the spectral simulation of the powder-pattern TRESR spectrum. In our previous study, the sign of the MPC in the VVD film could be understood by assuming the collision between the trapped triplet exciton ($^3\text{ex}_t$) and mobile carrier (^2c). In this work, we measured the temperature dependence of the single TRESR transition in order to justify the collision to the trapped triplet exciton ($^3\text{ex}_t$), that is, the majority of the triplet excitons are trapped, and to estimate the depth of the trap in the Py/DMPI VVD film. Figure 8(a) shows the typical single-crystal TRESR at 297 K observed at a magnetic field direction displaced from the symmetry axis. The corresponding TRESR spectra observed at each temperature are given in the supporting information (Fig. S4). We chose a magnetic field direction to observe the single TRESR transition, which is displaced from the symmetry axis, as it is not necessary to identify the relation between the direction of the external magnetic field and the crystal axis. A clear signal corresponding to the microwave absorption was observed at room temperature (Fig. 8(a)). The signal intensity decreased with decreasing temperature (see Fig. S4). Figure 8(b) shows the temperature dependence of the integrated signal intensity for the single TRESR transition. TRESR signal is owing to the mobile triplet exciton, because the line-shape was Lorentzian. The line-width of the triplet exciton itself is not changed significantly (see Fig. S4). However, in their mobile triplet exciton, the motional narrowing occurs as shown by the Lorentzian line-shape, which leads to a higher signal peak. When the exciton is trapped, the line-width is expected to be suddenly broaden. The trap state may be out of the sensitivity of the present detection. Therefore, the signal decrease can be reasonably expected by the localization of the mobile exciton to the trap state. The temperature dependence of the signal intensity was analyzed using the Arrhenius equation. The E_{trap} value was determined to be $640 \pm 89 \text{ cm}^{-1}$ ($E_{\text{trap}}/k_B = +921 \pm 128 \text{ K}$) using a least-squares fit. The observed data do not really follow well in the Arrhenius equation using a single exponential function, indicating the multiple trap sites with deferent depth. Although the better fit was possible when the multi exponential function was used (not shown), we use the above E_{trap} value in the later discussion, because the value obtained as a single exponential Arrhenius equation means the representative depth of their traps. The line-shape of the TRESR signal at 300 K was analyzed by a 100% Lorentzian function, showing that the observed signal originated from the mobile excitons (^3ex), which were released from the trap by thermal excitation. Therefore, the depth of the exciton trap (E_{trap}/k_B) was estimated to be approximately

1000 K. The depth is much larger than 300 K, which suggests that many triplet excitons are trapped even at room temperature. Our findings support the assumption of the collision to the trapped triplet exciton ($^3\text{ext}_t$) that was made in our previous work. Thus, the collision model between the trapped triplet exciton ($^3\text{ext}_t$) and mobile carrier has been confidently justified.

V. CONCLUSIONS

Low-field MFE and EDMR measurements of the photocurrent in the VVD films of a CT complex (Py/DMPI) were carried out using the custom-made interdigitated platinum electrode made on a quartz substrate. Re-examination of the photocurrent and MFE was conducted in the range of 3–200 mT. The temperature dependence of the photocurrent, EDMR, and TRESR signal intensities was examined. In the measurement of low-field MFE, a small dip was observed at approximately 0.3 mT. This behavior was simulated by solving the simultaneous Liouville equations of the density matrix for the stepwise hopping model of the DD pair. The effective hyperfine couplings in this CT system were determined from the dip magnetic field with the help of the simulation. Our findings show confidently that the observed low-field MFE is the low-field effect due to the hyperfine interaction,^{23 24 25 26 27 28} leading to the radical-pair ISC within the DD pair. Furthermore, the two types of collision mechanisms (DD and TD models) are strongly supported. Direct evidence of weakly coupled electron-hole pairs, which dissolve into mobile carriers, was obtained through the EDMR signal. The effective activation energies required for separation from the photoinduced CT state (D^+-A^-) to the mobile carries were evaluated to be between 1182–1877 cm^{-1} ($\Delta E/k_B = 1700 - 2700$ K). The depth of the exciton trap (E_{trap}) was estimated to be $640 \pm 89 \text{ cm}^{-1}$ ($E_{\text{trap}}/k_B = +921 \pm 128$ K), which is much greater than the thermal activation energy at 300 K, supporting the majority of the trapped triplet exciton ($^3\text{ext}_t$) assumed in the TD model of our previous work. In this work, Py/DMPI was chosen as a typical weak CT complex due to its well-defined molecular stoichiometry and donor and acceptor properties. Although the photocurrent behavior was previously described, in-depth knowledges (low-field MFE, the mechanism, the depth of the exciton trap, and the effective activation energy) were obtained in this work. A protocol to analyze the excited-state dynamics of the weak CT complexes in solid-phase can be summarized as follows. (1) Use of the interdigitated platinum electrode made on quartz substrate is convenient tool for studying the semiconducting materials with high impedance. (2) MFE of the photocurrent provides the powerful information to clarify the dynamics of the photo-generated carrier in the devices. (3) EDMR and TRESR measurements and

their temperature dependence can provide the information of the activation energy and trap depth as well as the MFE mechanisms. (4) The simulation of the MFE based on the stochastic Liouville equations gives the detail knowledge of their carrier dynamics. This protocol has been demonstrated in the typical weak CT complex. Although the each measurement method and the material used in this work are already reported, the combination between their measurements and theoretical simulation can be demonstrated as a powerful tool to clarify the carrier dynamics in the devices using the organic CT complexes, which are important materials providing continuing progress.^{5 6}

7

SUPPLEMENTARY MATERIALS

See supplementary materials for the spectrum responsibility of VVD films, the photocurrent response at 1 voltage bias of 10 V, the temperature dependence of EDMR spectra, the temperature dependence of TRESR spectra, and the estimation of kinetic constants in Table 1.

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APPENDIX:

The simultaneous Liouville equations of the density matrix for the DD mechanism are given by equations (4) – (6). As already mentioned, the effective isotropic hyperfine-couplings, a_{D0}^{eff} and a_{Dm}^{eff} were varied to reproduce the observed dip position and the overall MPC in the low-field region. The fine-structure parameter D of the closest contact pair is -0.0141 cm^{-1} , which was evaluated from the data of the charge-separated triplet state of Py/PMDA (pyrene/dimethylpyromellitic-dianhydride), because the distance between the donor and acceptor is almost same as that of Py/DMPI (0.368 nm for Py/DMPI and 0.363 nm for Py/PMDI) and the packing form is also resemble to each other.²¹ The D values of the second, and third neighbor contact pairs were estimated by equation (A1) using the distance obtained by the X-ray crystallographic structure.²¹

$$D = -\frac{3\mu_0}{8\pi} \frac{(g\beta)^2}{\langle r^3 \rangle} \quad (\text{A1})$$

The fine-structure parameter, E , of each pair was approximated to be zero. In addition, the relative orientations among the fine-structure tensors of each neighbor contact were ignored because of minimal influence on the MFE. Thus, the principal axis of all fine-structure tensors was approximated to be collinear to each other. J_{D0Dm} is the exchange interaction between the D0 and Dm sites. The exchange interaction of the nearest neighbor contact pair of D0 and D1 sites is expected to be large enough because of the overlap of their wavefunctions. Therefore, we set this value to be $J_{D0Dm}/h = -1.0 \times 10^{12} \text{ Hz}$. In contract, the exchange interaction of D0 to D3, D4, ... D8 sites is expected to be very small according to the X ray crystallographic structure of Py/DMPI single crystal (see in ref. [21]) because of the negligible overlap of their wavefunctions. Therefore, we set these values to be zero. The sign and magnitude of the exchange interaction of D0 – D2 pair are unknown parameter required in the simulation. In the solution or donor-acceptor covalently linked systems, the magnitude and sign of the exchange interaction ($2J$) can be determined in weakly coupled radical pairs using TREPR.^{37–38} However, in the present weak CT system, the dissociation of the CT complex occurs in the solution and TRESR signal in the solid phase is dominated by the triplet-exciton. In addition, transient absorption measurement in the CT polycrystalline powder sample is difficult, although such measurement can give more precise estimation of the kinetic constants.³⁹ Therefore, the experimental determination of the J value was difficult. However, the sign could be determined to be ferromagnetic ($2J > 0$) from the comparison of the observed and simulated MFE curvatures (see Fig. S7). We varied the exchange interaction of weakly coupled D0 – D2 pair as the fitting parameter

to reproduce the low-field MPC.

$\rho_{D0D1}(0)$ is the initial condition at time zero, which is the density matrix of the geminate D0–D1 pair. The selective population to the singlet spin configuration was assumed as the $\rho_{D0D1}(0)$, because the charge separated singlet excited states, ($^1(D^+ - A^-)$), are effectively generated by the direct photoexcitation of the CT band in such weak CT complex. In the calculation, we chose the weak coupled (WC) basis, which is written as $|S_{D1}, m_{D1}\rangle |S_{Dm}, m_{Dm}\rangle$. The electron spin part of initial density matrix, $\rho_{D0D1}(0)_{el}$, is given by:

$$\rho_{D0D1}(0)_{el} = |S\rangle\langle S| = U_{S(S+1)\rightarrow WC} \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} U_{S(S+1)\rightarrow WC}^\dagger \quad (A2) ,$$

The initial density matrix of the electron and nuclear spin states is expressed as follow:

$$\begin{aligned} \rho_{D0D1}(0) &= \rho_{D0D1}(0)_{el} \otimes (\text{nuclear spin part}) \\ &= \rho_{D0D1}(0)_{el} \otimes \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}_{ID0} \otimes \begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}_{ID1} \end{aligned} \quad (A3)$$

$U_{S(S+1)\rightarrow WC}$ is the unitary transformation matrix from the eigenfunction basis of $\hat{S}^2$ operator to the WC basis.

The simultaneous Liouville equations (4) – (6) were rewritten into a single equation in the Liouville space as follows:

$$\frac{d}{dt} \rho_{DD}^L(t) = k_0 \rho_{DD}^L(0) - (L_{DD} + K_{DD}) \rho_{DD}^L(t), \quad (A4)$$

where

$$\rho_{DD}^L(t) = \begin{pmatrix} \rho(t)_{D0D1}^L \\ \rho(t)_{D0D2}^L \\ \vdots \\ \rho(t)_{D0Dn}^L \end{pmatrix} \quad (A5) ,$$

and

$$\rho_{D0Dm}^L(t) = \begin{pmatrix} \rho(t)_{D0Dm\ 11} \\ \rho(t)_{D0Dm\ 12} \\ \vdots \\ \rho(t)_{D0Dm\ 44} \end{pmatrix} \quad (A6).$$

The Liouville operator of the Hamiltonian matrixes is given by:

$$L_{DD}(t) = \begin{bmatrix} L_{D0D1}(t) & \mathbf{0} & \cdots & \mathbf{0} \\ \mathbf{0} & L_{D0D2}(t) & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{0} & \mathbf{0} & \cdots & L_{D0Dn}(t) \end{bmatrix} \quad (A7),$$

and

$$L_{D0Dm}(t) = \frac{i}{\hbar} (H_{D0Dm} \otimes E - E \otimes H_{D0Dm}^*) \quad (A8)$$

Here, $\mathbf{E}$ is the 16×16 unit matrix. The matrix of the rate constants ($\mathbf{K}_{DD}$) is expressed by:

$$\mathbf{K}_{DD} = \begin{bmatrix} k_1 \mathbf{E} & -k_{-1} \mathbf{E} & \cdots & \mathbf{0} \\ -k_1 \mathbf{E} & (k_1 + k_{-1}) \mathbf{E} & \cdots & \mathbf{0} \\ \mathbf{0} & \vdots & \ddots & \vdots \\ \mathbf{0} & \mathbf{0} & \cdots & (k_1 + k_{-1}) \mathbf{E} \end{bmatrix} \quad (\text{A9}).$$

In the steady-state approximation of $d\rho_{DD}(t)/dt = 0$, the solution of the density matrix is solved as follows:

$$\rho_{DD}^L = k_0 (\mathbf{L}_{DD} + \mathbf{K}_{DD})^{-1} \rho_{DD}^L(0), \quad (\text{A10})$$

The photocurrent is generated from the charge-separated electron-hole pair with negligible interaction, thus, the long-distance separated pair (the n -th neighbor contact pair (D0–D n pair) in the stepwise hopping model shown in Figure 6(c)). Therefore, the efficiency of the photocurrent generation, in which the external magnetic field is applied to the (θ, ϕ) direction to the principal axes (X, Y, Z) of the fine-structure tensor, can be calculated using the local density matrix of the n -th neighbor contact pair (ρ_{D0Dn}) as follows:

$$\phi_{DD}(B, \theta, \phi) = (k_1/k_0) \text{Tr}(\rho_{D0Dn} \mathbf{E}) = (k_1/k_0) \text{Tr}(\rho_{D0Dn}). \quad (\text{A11})$$

Since the molecules are oriented randomly in the sample, the averaged MC effect is given by:

$$\langle \phi_{DD}(B) \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi \phi_{DD}(B, \theta, \phi) \sin \theta \, d\theta \, d\phi \quad (\text{A12})$$

The efficiency of the MPC (%) arising from the DD mechanism is given by:

$$\text{MPC} = \frac{\langle \phi_{DD}(B) \rangle - \langle \phi_{DD}(0) \rangle}{\langle \phi_{DD}(0) \rangle} \times 100 \quad (\text{A13}).$$

Figure 9(a) shows the dependence of the simulated MPC ratio on numbers (n) of the interacting sites taken in the simulation. As increasing n , the MPC ratio is increased. The saturated value was ca. +2.7% as shown in Figure 9(b). In the case of $n = 8$, the value (+2.3% at 20 mT) was close to the saturated value, although the slight difference of 0.4% remained. Therefore, we adopted the simulated curve of $n = 8$ to use in the comparison with the observe MPC ratio. The spin Hamiltonian parameters and kinetic constants used in the simulation of the low-field effect (blue curve in Fig. 5) are summarized in the following Tables. The MFE ratio does not depend on the excitation rate constant k_0 . Therefore, we can choose the value freely. Here, we set $k_0 = 1.0 \times 10^8 \text{ s}^{-1}$, which is the same value as the dissociation kinetic constant of the DD pair. We measured the life-time of D0-D1 pair (geminate $\text{D}^+\text{-A}^-$ pair generated by the excitation) by the time-resolved emission spectroscopy (see Fig. S5). In this experiment, we could

estimate the sum of the rate constant ($k_S + k_T$) to be ca. $1.0 \times 10^8 \text{ s}^{-1}$. The magnitude of the MFE is sensitive to the ratio, k_T/k_S (see Fig. S6). Therefore, k_S and k_T were evaluated to be $4.2 \times 10^7 \text{ s}^{-1}$ and $5.8 \times 10^7 \text{ s}^{-1}$ ($k_T/k_S = 1.4$), respectively, by the comparison with the observed MFE. The details of the estimations of the kinetic constants and other parameters are given in the supporting information.

Table 1 Kinetic constants used for the simulation of the green curve in Figure 5. The rate constants of the case of $k_T/k_S = 1.4$ are shown in this Table.

	k_0	k_1	k_{-1}	k_S	k_T
Kinetic Const.	$1.0 \times 10^8 \text{ s}^{-1}$	$1.0 \times 10^8 \text{ s}^{-1}$	$1.0 \times 10^8 \text{ s}^{-1}$	$4.2 \times 10^7 \text{ s}^{-1}$	$5.8 \times 10^7 \text{ s}^{-1}$

Table 2 Spin Hamiltonian parameters used for the simulation of the green curve in Figure 5.

	g value	a^{eff} / Hz
D0 site	2.003	-26×10^6
Dm site	2.003	-14×10^6

Table 3 Fine-structure parameters calculated by Eq. (A5), and J values used for the simulation of the green curve in Figure 5.

DD Pairs	D0 – D1	D0 – D2	D0 – D3	D0 – D4	D0 – D5	D0 – D6	D0 – D7	D0 – D8
D / cm^{-1}	-0.0141	-0.00782	-0.00201	-0.00150	0.0	0.0	0.0	0.0
E / cm^{-1}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$h^{-1}J / \text{Hz}$	-1.0×10^{12}	$+7.0 \times 10^7$	0.0	0.0	0.0	0.0	0.0	0.0

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Figure Captions

FIG.1 Molecular Structures of Pyrene and DMPI

FIG.2 Excited-state and carrier dynamics in VVD film of Py/DMPI and expected energy-level location. (a) Excited-state and carrier dynamics owing to MPC in our previous work.¹⁹ (b) Energy level location and activation energies.

FIG.3 Photocurrent response under 10 V bias (a) and its temperature dependence (b) of Py/DMPI VVD films.

FIG.4 MPC of Py/DMPI VVD film. Red: MPC data obtained in 3–200 mT (after conversion by Eq. (3)). Black: MPC data obtained in 0–10 mT.

FIG.5 Low-field MPC of Py/DMPI VVD films and simulation. (a) Black: Observed MPC data obtained in 0–10 mT. Blue: Low-field MFE simulation at $k_T/k_S = 1.4$ using stepwise DD model. Red: Low-field MFE simulation at $k_T/k_S = 1.5$. (b) Residual between the observed data and blue curve.

FIG.6 Stepwise hopping model of carrier. (a) Migration of the charge carriers in the CT crystals. (b) Picture of the deactivation to the ground state and intersystem crossing (ISC). Charge recombination (CR) to the ISC to the triplet excitonic state of pyrene are assumed to occur only from the nearest neighbor contact pair $^{1,3}(D^+-A^-)$ generated by the photoinduced charge separation. (c) Schematic picture of the stepwise hopping model.

FIG.7 EDMR signal of the Py/DMPI VVD film and shape analysis. (a) Observed EDMR signal obtained at 300K by monitoring the photocurrent. Lines: Lorentzian fit. (b) Temperature dependence of the signal intensity. Inset shows the mechanism of the EDMR signal generation.

FIG.8 Typical single crystal TRESR spectrum of Py/DMPI and temperature dependence of the signal intensity. (a) Observed single transition signals at 297 K. The inset shows the whole spectrum in the wide range of the magnetic field. Black curve is the observed data and the red curve is the Lorentzian fit of the line-shape. (b) Temperature dependence of the signal intensity.

FIG. 9 Dependence of the simulated MPC ratio on number (n) of the interacting sites. Simulated MPC curves. (b) Plot of the values at 20 mT vs. site numbers taken into accounts. The curve was well fitted by a function: $f(n) = a(1 - b \exp(-cn))$. Here, $a = 2.8$, $b = 1.36$, and $c = 0.25$ were determined by the least-squares fit. Therefore, the saturated value of the MPC ratio was estimated to be 2.8%.

(a)

(b)

Supplementary Material for “Low-Magnetic Field Effect and Electrically Detected Magnetic Resonance Measurements of Photocurrent in Vacuum Vapor Deposition Films of Weak Charge-Transfer Pyrene/Dimethyl- pyromellitdiimide (Py/ DMPI) Complex ”

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1. Spectrum Responsibility of VVD films (Py/DMPI)

The transmission spectrum of the VVD film of Py/DMPI is shown in Figure S1, which was measured by a UV/Vis/NIR spectrometer (SHIMADZU UV-3600). The excitation wavelength dependence of the photocurrent response was also measured using band-pass filters (Edmund Optics, CWL, 12.5 mm Dia. Hard Coated OD4 50 nm band-pass filter).

FIG. S1 Transmission spectrum and wave-length dependence of the photocurrent of the Py/DMPI VVD film. Black curve is the transmission spectrum. Sticks are photocurrent response. The maximum values of the photocurrent are divided by the light power after each band-path filter.

2. Photocurrent Response at a Voltage Bias of 10 V

FIG. S2 Photocurrent response under 1.5 V bias (a) and its temperature dependence (b) of Py/DMPI VVD films.

3. Temperature Dependence of EDMR Spectra and Their Lorentzian Fit

FIG. S3 Observed EDMR signal of the Py/DMPI VVD film at each temperature obtained by monitoring the photocurrent. Red lines are their Lorentzian fit.

4. Temperature Dependence of TRESR Spectra and Their Lorentzian Fit

FIG. S4 Observed TRESR signal of the Py/DMPI single crystal at each temperature. Red lines are their Lorentzian fit.

5. Estimation of Kinetic Constants in Table 1

The dissociation kinetic constant (k_1 and k_{-1}) was estimated to be ca. $1.0 \times 10^8 \text{ s}^{-1}$ by the lifetime (τ) evaluated from the linewidth (δH) of the steady-state EDMR using the relation of $\delta H \sim \hbar/g\mu_B\tau$. k_S and k_T were estimated from the lifetime of the geminate $D^+ \cdot A^-$ pair (D0-D1 pair) generated directly by the excitation with the help of the dependency of the MFE on their magnitude and k_S/k_T ratio.

i) Estimation of Kinetic Constants of k_1 and k_{-1}

EDMR signal can be generated by the ESR in the triplet spin-sublevels of the weakly coupled DD pair, in which one is the cation radical of pyrene and another is the anion radical of DMPI and they are not the closest pair (D0 – D1). The D0 – D2 pair and/or D0 – D3 pair in Fig.6 are the candidate of the EDMR responsible weakly coupled DD pair. The line shape was Lorentzian by the motional narrowing, showing no inhomogeneous broadening. Therefore, the intrinsic lifetime can be estimated from their line width. The lifetimes are determined by the sum of the dissociation rate constants ($k_1 + k_{-1}$) and the spin-lattice and spin-spin relaxation time. From the linewidth ($\delta H = 1.4 \text{ mT}$) of the EDMR signal shown in Fig.7, the lifetime (τ) of the DD pair can be estimated to be $4.0 \times 10^{-9} \text{ s}$ using relationship of $\delta H \sim \hbar/g\beta\tau$. The spin relaxation time is safely expected to be much longer than $4.0 \times 10^{-9} \text{ s}$ and the line-shape was Lorentzian. Therefore, the short lifetime is due to the dissociation of the DD pair. There is no reason of the difference between k_1 and k_{-1} . Therefore, the kinetic constants were estimated to be $k_1 = k_{-1} = 1.0 \times 10^8 \text{ s}^{-1}$ ($k_1 + k_{-1} \sim 1/\tau = \text{ca. } 2.5 \times 10^8 \text{ s}^{-1}$).

ii) Estimation of Kinetic constants of k_S and k_T

In order to evaluate the kinetic constants of k_S and k_T , we carried out the time-resolved emission spectroscopy of Py/DMPI polycrystalline powder under the zero-bias condition at room temperature. In the zero-bias condition, the photocurrent is negligible, and the excitation was carried out using the light of $\lambda_{ex} = 355 \text{ nm}$ (not CT band excitation). Figure S5 shows the time-resolved emission spectra of Py/DMPI polycrystalline powder together with those of pyrene powder sample and their time-courses at the wavelength at each signal peak. In the Py/DMPI sample, a broad emission with the peak at $\lambda_{em} = 540 \text{ nm}$ was observed as shown in Fig. S5(a). The emission lifetime was determined to be 10.7 ns by the decay fitting using the equation, $I(t) = I_0 + A \sum_{i=1}^{11} I_i^{\text{IRF}} \times \exp(t - t_i^{\text{IRF}}) / \tau$, given in Fig. S5(c) taking the instrument response function into account. This emission band is appeared at the longer wavelength than the excimer emission of pyrene¹ and the lifetime was shorter than 18.8 ns of pyrene (Fig. S5(b)). Therefore, this

emission can be assigned

FIG. S5 Time resolved emission spectra of Py/DMPI polycrystalline powder and Pyrene powder samples at room temperature. (a) Emission spectra (left) of Py/DMPI powder at 15 ns after excitation laser peak and the time course (right) at the emission peak ($\lambda_{em} = 540$ nm). Black points are observed data. Red line is the least-square fitting using the function $I(t)$ in (c). Gray plots are the data of the instrument response function (IRF), which was obtained from the spectral data around $\lambda_{em} = 355$ nm (excitation laser wavelength). (b) Emission spectra (left) of pyrene powder at 5 ns after excitation laser peak and the time course (right) at the emission peak ($\lambda_{em} = 472$ nm). (c) IRF and the fitting function $I(t)$. The histograms show the data of I_i^{IRF} .

to the emission from the excited CT complex, $^1(\text{D}^+-\text{A}^-)$ in Fig. 2(a) (D0-D1 pair in Fig. 6). The charge separation in the present system is not efficient under the applied voltage bias, because the magnitude of the photocurrent in the present system is small. This may come from the energy carrier between $^1(\text{D}^+-\text{A}^-)$ state and the weakly coupled D0-D2

pair. Therefore, the lifetime of $^1(\text{D}^+-\text{A}^-)$ state is expected to be dominated by the sum of the rate constants of k_S and k_T under the zero-bias condition. Therefore, in this experiment, we could estimate the sum of the rate constant ($k_S + k_T$) to be $\text{ca. } 1.0 \times 10^8 \text{ s}^{-1}$ from the lifetime (10.7 ns). In order to evaluate each rate constant, we checked the dependence of the simulated MFE on the ratio, k_T/k_S as shown in Fig. S6. As pointed out by Ikoma *et al.*,² positive MPC was simulated when $k_T > k_S$, the observed MPC of $\text{ca. } 2.3\%$ increase of the photocurrent at 10 mT locates between $1.0 < k_T/k_S < 2.0$. When $k_T/k_S = 1.4$ and other parameters except k_S and k_T are the values shown in Table 1 – Table 3, the simulated MFE curve was resemble in the magnitude to the observed one shown in Fig. 5. This ratio was close to $k_T/k_S = 1.7$ estimated in our previous work,³ which was estimated from the MFE simulated in the middle field region. Therefore, k_S and k_T were evaluated to be $4.2 \times 10^7 \text{ s}^{-1}$ and $5.8 \times 10^7 \text{ s}^{-1}$ ($k_T/k_S = 1.4$), respectively, by the comparison with the observed MFE. This ratio is reasonable one because both the luminescence from the D0–D1 pair ($^1(\text{D}^+ - \text{A}^-)$) and triplet exciton ($^3(\text{D}^* - \text{A})$) were clearly observed in Py/DMPI CT complex.

FIG. S6 k_T/k_S dependence of MPC ratio. $k_S + k_T = 1.0 \times 10^8 \text{ s}^{-1}$ Other parameters except k_S and k_T are the values shown in Table 1 – Table 3.

6. Estimation of J values

As described in the main text, the exchange interaction of the nearest neighbor contact pair (D0–D1 pair) is expected to be large enough because of the overlap of their wavefunctions. The sign should be antiferromagnetic, although the choice of the opposite sign, ferromagnetic J , gave the same result of the MPC simulation, because D0–D1 pair with very large J did not directly contribute to the MPC effect. Therefore,

we set this value to be $J_{D0Dm}/h = -1.0 \times 10^{12}$ Hz. In contract, the exchange interaction of D0 to D3, D4, ... D8 sites is expected to be very small according to the X ray crystallographic structure of Py/DMPI single crystal (see in ref. [21]). The sign and magnitude of the exchange interaction (J) of D0 – D2 pair is unknown parameter required in the simulation. The experimental determination of the J value was difficult in the present weak CT system, because of the dissociation of the CT complex in the solution, the triplet exciton observed in the solid-state TRESR signal, and difficulty of transient absorption measurement in the CT polycrystalline powder sample, although such measurement can give more precise estimation of the kinetic constants.⁶ Therefore, we evaluated the J value using the J dependency of the MPC simulation. Figure S7 shows the sign dependency of the MPC simulation. When the magnitude of J value of D0–D2 site were varied, the ratio over 2% at 10 mT was expected for $J_{D0-D2}/h = +1.0 \times 10^7$ Hz – $+1.0 \times 10^8$ Hz. The sign could be determined to be ferromagnetic ($2J > 0$) by the comparison of the observed and simulated MFE curvatures (see Fig. S7). We varied the exchange interaction of weakly coupled D0 – D2 pair as the fitting parameters to reproduce the low-field MPC. Figure 8 shows the detailed magnitude dependence of the J value of D0 – D2 pair. From the magnitude and curve dependence of the simulated

MPC, we chose the J value to be $J_{D0D2}/h = +7.0 \times 10^7$ Hz.

FIG. S7 Sign dependence of J value to the MPC ratio. Other parameters except the J value of D0 – D2 pair are the values shown in Table 1 – Table 3.

FIG. S8 J value dependence of the MPC ratio. Other parameters except the J value of D0 – D2 pair are the values shown in Table 1 – Table 3.

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